

Polymer chain collapse induced by the many-body dipole correlations

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We present a simple analytical theory of flexible polymer chain dissolved in a good solvent, carrying the permanent freely oriented dipoles on the monomers. We take into account the dipole correlations within the random phase approximation (RPA), as well as a dielectric heterogeneity in the internal polymer volume relative to a bulk solution. We demonstrate that the dipole correlations of monomers can be taken into account as pairwise only when the polymer chain is in a coil conformation. In this case the dipole correlations manifest themselves through the Keesom interactions of the permanent dipoles. On the other hand, effect of the dielectric heterogeneity (dielectric mismatch effect) leads to effective interaction between the monomers of the polymeric coil. Both of these effects can be taken into account by the renormalization of the second virial coefficient of the volume interactions monomer-monomer. We establish that in the case when the solvent dielectric permittivity exceeds the dielectric permittivity of polymeric material, the dielectric mismatch effect competes with the dipole attractive interactions, leading to a polymer coil expansion. In the opposite case both dielectric mismatch effect and dipole attractive interaction lead to the polymer coil collapse. We analyse a coil-globule transition caused by the dipole correlations of monomers within a many-body theory. We demonstrate that accounting for the dipole correlations higher than pairwise smooths this pure electrostatics driven coil-globule transition of the polymer chain.

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I. INTRODUCTION

A coil-globule (CG) transition in dilute polymer solutions is very important phenomenon for the various technological advances, ranging from the polymer functionalizations (such as polymerization, plasticization, dyeing, etc.) in chemical industry to encapsulation of the drug compounds into the polymer globules and their subsequent targeted delivery in pharmaceutical applications. Therefore, technological importance of the CG transition attracts great attention of many researchers both theorists and experimentalists in soft matter physics during the last few decades. Till now great efforts have been made in development of CG transition theory. Existing theoretical models made a great contribution to an understanding of this phenomenon¹⁻¹⁷. The classical theoretical models¹⁻⁶ of the CG transition are based on the idea that decreasing of the solution temperature below certain threshold value (theta-temperature) leads to the domination of the attractive interactions between the monomers and, thus, to the collapse of a polymer coil. Such a simple idea allows one to rationalize the conformational behavior of the real synthetic polymer chains in the solvent media.

It is well known from the experiments (see, for instance,^{18,19}) and MD simulations²⁰⁻²³, that in the dilute polyelectrolyte solutions in the regime of good solvent the CG transition of the flexible polyelectrolyte chain can take place. This unconventional CG transition of the polyelectrolyte chain is accompanied by the condensation of the counterions onto the polymer backbone. Therefore, this CG transition has a pure electrostatic nature. Due to the fact that this electrostatic conformational transition takes place in the regime of good solvent, i.e., when the polyelectrolyte chains are well soluble, we cannot use the mentioned above classical models of the CG transition and, consequently, the concept of theta-temperature to describe it theoretically.

Till now two possible mechanisms of this electrostatic CG transitions have been proposed. The first mechanism (see references^{24,25}) is based on the idea that the polymer chain collapse is caused by counterion electrostatic correlations²⁶. More specifically, when the electrostatic interactions become strong enough, the counterions favor to adsorb onto the polymer surface, neutralizing the macromolecule charge. In this mechanism the counterions are not strongly bounded with the monomers, but can move freely along the polymer backbone. Despite the full neutralizing of the macromolecule charge due to the counterion condensation²⁷,

the thermal fluctuations of the charge density near its zero value are unavoidable. These charge density fluctuations, in turn, lead to cooperative mutual attraction of monomers (so-called Kirkwood-Shumaker interaction^{28,29}), causing the CG transition. It is worth noting that such correlation attraction of like-charged particles can cause the phase separations in colloid and polyelectrolyte solutions (see, for instance,^{30,31}). Due to the fact that this CG transition takes place at large enough Coulomb strength (characteristic electrostatic energy expressed in thermal energy units²⁵) to take into account the electrostatic effects, it is necessary to go beyond the classical Debye-Hückel (DH) theory. A successful attempt to describe this electrostatic CG transition beyond the DH theory was undertaken in ref.²⁴ In this work the counterions immersed into the background of the polymer chain charge were considered within the one component plasma (OCP) model²⁶, using the precise relation for its electrostatic free energy³². It is worth noting that accounting for the electrostatic correlations of counterions within the OCP model allowed one to rationalize the relations for the radius of gyration of the polyelectrolyte chain as a function of the Coulomb strength obtained from the MD simulations²⁰.

The second mechanism is based on the assumption that this CG transition takes place due to the attractive interaction of the thermally fluctuating dipoles, appearing along the polymer backbone due to the counterion condensation. This mechanism was first proposed in reference³³ and later discussed in details in references^{34,36}. However, within all mentioned above theories dipole correlations were considered as pairwise. Indeed, in the works^{33,36} an influence of the dipole correlations on the polymer chain conformation was accounted by the renormalization of the second virial coefficient attributed to the volume interactions between monomers. In the references^{34,35} the dipole correlations have been taken into account using the Keesom pair potential. As it was recently showed in the ref.⁴⁴, dipole correlations of monomers can be considered as pairwise only when the polymer chain is in a coil state. However, when the polymer chain is in the globular conformation, electrostatic dipole correlations must be taken into account at the many-body level. Therefore, many-body electrostatic correlations might play a crucial role in the "dipole" mechanism, as well as in the above discussed "Coulombic" mechanism of the polyelectrolyte chain collapse.

Physically, in real polyelectrolyte solutions both Coulombic and dipole scenarios of the CG transition could be realized. It depends mostly on the chemical specifics of the monomers and counterions. Thus both of these mechanisms should be thoroughly analyzed from the

first principles of statistical mechanics. However, to the best of our knowledge, the analysis of the dipole mechanism of the CG transition in the dilute solutions of the electrically neutral polar polymers, regarding to the many-body dipole correlations has not been available in the literature till now.

On the other hand, statistical physics of dielectric polar polymers remains one of the most undeveloped areas of polymer physics. Indeed, only several theoretical works have been published till now, where thermodynamic and structural properties of dielectric polymers in the bulk solution without^{35,37-42} and with^{43,44} an electric field application have been discussed. In ref.³⁷ Podgornik studied within the Feynman path integrals formalism the behavior of electrostatic persistence length of semi-flexible polymer chain whose monomers interact through a screened dipolar interaction potential. In ref.³⁵ Kumar et al. within the Edwards-Singh method calculated the mean-square radius of gyration of polyzwitterionic molecules in aqueous solutions in dependence on the different physico-chemical parameters, such as the chain length, electrostatic interaction strength, added salt concentration, dipole moment, and degree of ionization of the zwitterionic monomers. In ref.³⁸ the polarizing many-body correlations at the level of random phase approximation (RPA) were taken into account. Thereby, it was shown that the latter lead to ordering of the semi-flexible anisotropic polymer chains in the solution. In ref.³⁹ Kumar et al. showed by means of the field-theoretic formalism that interactions between monomeric dipoles in polymer blends lead to considerable enhancement of the phase segregation. Lu et al. calculated within the field-theoretic formalism the interaction potential between two rigid polymers polarizable along their backbone in dependence on their mutual orientation⁴⁰. In ref.⁴¹ authors formulated a statistical field theory of the dielectric soft matter. In recent works the conformational behavior of the polarizable flexible polymer chain under the external electric field within the pure mean-field theory⁴³ and theory with account for the many-body dipole correlations of monomers⁴⁴ was investigated. It was shown that in both theories regardless of the polymer chain conformation (coil or globule) increasing the electric field results in the polymer chain expansion (electrostriction). It was also shown that the strong enough electric field in the regime of poor solvent can induce the globule-coil transition of the polarizable polymer chain due to the electrostriction effect.

In this paper we present a simple analytical self-consistent field theory of flexible polymer chain carrying the permanent freely oriented dipoles on the polymer backbone dissolved in

a good solvent. We take into account the many-body dipole correlations within RPA, as well as effect of the dielectric heterogeneity near the polymer backbone relative to the bulk solution. We provide an analysis of the conformational behavior of the polar electrically neutral polymer chain with account for the dipole correlations of monomers at the many-body level.

The paper is organized as follows: the theoretical background is presented in section 2, some analytical evaluations – in section 3, numerical results and discussion – in section 4, and concluding remarks – in section 5. At the end of paper the Appendix with some supplementary mathematical details is placed.

II. THEORY

We consider a dielectric flexible polymer chain with the degree of polymerization N dissolved in a dielectric solvent with the permittivity ε_s . Let each monomer segment of the polymer chain carry the permanent freely oriented dipole moment \mathbf{p}_j ($j = 1, \dots, N$) (see Fig. 1). The latter may be realized for a weak polyelectrolyte chain in the regime of counterion condensation, when the counterions and monomers form the strongly bounded ion pairs²⁷ or for the polyzwitterionic macromolecules³⁵. Moreover, such situation can also be realized for the non-polar synthetic polymers which purchased the polar groups on the monomers due to some chemical modifications. For the sake of simplicity in this study we shall neglect the polarizability effect attributed to the fluctuations of the absolute value of the dipole moments. As one can show, accounting for this effect will not change the final outcomes. To study the conformational behavior of the polymer chain, we formulate a simple Flory-type⁵³ self-consistent field theory, considering the radius of gyration R_g as a single order parameter. Therefore, we assume that the polymer chain occupies the volume which can be estimated by the volume of gyration $V_g = 4\pi R_g^3/3$.

The total solvation free energy of the polymer chain can be written as a sum of three terms

$$F(R_g) = F_{conf}(R_g) + F_{vol}(R_g) + F_{el}(R_g), \quad (1)$$

where $F_{conf}(R_g)$ is the conformation free energy of the ideal polymer chain which can be

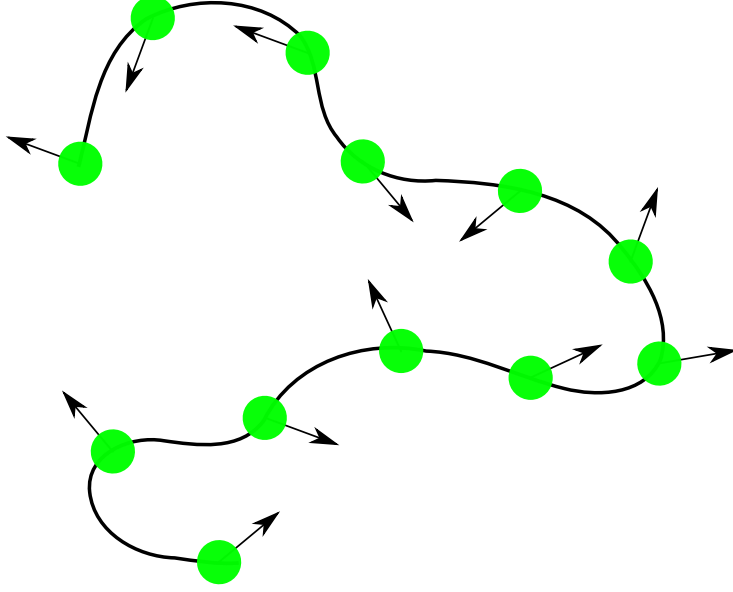


Figure 1. Illustration of the flexible polymer chain with permanent freely oriented dipole moments distributed along its backbone.

estimated by the following interpolation formula^{2,54,55}

$$F_{conf}(R_g) = \frac{9}{4}k_B T (\alpha^2 + \alpha^{-2}), \quad (2)$$

where $\alpha = R_g/R_{0g}$ is the expansion factor, $R_{0g}^2 = Nb^2/6$ is the mean-square radius of gyration of the Gaussian polymer chain, b is the Kuhn length, k_B is the Boltzmann constant, T is the temperature. To take into account the volume interactions of monomers, we use the Flory-Huggins (FH) relation for excess free energy of the polymer chain in the solvent^{12,53,56}

$$F_{vol}(R_g) = \frac{V_g k_B T}{v} ((1 - \phi) \ln (1 - \phi) + \phi - \chi \phi^2), \quad (3)$$

where $\phi = Nv/V_g$ is the volume fraction of the monomers, $v = b^3$ is the effective monomer volume, χ is the Flory-Huggins parameter. In contrast to our previous works^{43,44}, in this study to take into account the volume interactions, we do not use the virial equation of state. Instead, we use the FH interpolation formula to consider the polymer chain conformational behavior in a wide range of the monomer volume fraction. In principle, to take into account the volume interactions between species, we might use any other interpolation formulas, such as Van der Waals equation of state (for example, see¹⁶). On the other hand, we chose FH formula due to the fact that it allows relate easily the solvent quality with parameters of volume interactions between species. It should be reminded that parameter χ determines the

effect of the Van der Waals interactions between species, excluding the interaction between the permanent dipoles, which we shall consider explicitly (see below). It should be noted that the concept of "disconnected" segments which was first introduced by I.M. Lifshitz (see original work⁶ and review⁷) allows us to construct the total free energy by using the different terms that are attributed to the conformational entropy of the polymer chain (eq. (2)) and volume interactions between monomers (eq. (3)).

In this case the electrostatic contribution to the free energy which is related to the thermal fluctuations of the permanent dipoles on the polymer backbone immersed to the dielectric background with permittivity ε can be calculated for the large enough gyration volume at the level of the random phase approximation (RPA) (see Appendix and^{38,44}):

$$F_{el}(R_g) \simeq \frac{2\pi k_B T V_g}{3v} \ln \left(1 + \frac{4\pi p^2 \phi}{3k_B T v \varepsilon} \right), \quad (4)$$

where ε is the reference dielectric permittivity of dielectric medium within the polymer volume which in general case must depend on the volume fraction of monomers. In present study, to take into account this dependence, we use one of the most simple interpolation formulas which was widely used in theoretical treatment of the polyelectrolyte solutions^{45–49}:

$$\varepsilon = \varepsilon_s + (\varepsilon_p - \varepsilon_s) \phi, \quad (5)$$

where ε_p is the reference permittivity of the polymeric material which is not related to the orientation fluctuations of the permanent dipoles, ε_s is the dielectric permittivity of solvent. Thus opposite to our previous works^{43,44}, where we put that dielectric permittivity in the internal polymer volume is the same as in the bulk, in present study we take into account the dependence of dielectric permittivity in the gyration volume on the solvent volume fraction.

Therefore, minimizing the total solvation free energy (1) with respect to the expansion factor α , after some algebra we arrive at the following equation

$$\begin{aligned} \alpha^5 - \alpha &= \frac{2\pi\sqrt{6}}{81} N^{3/2} \alpha^6 (-\ln(1-\phi) - \phi - \chi\phi^2) \\ &- \frac{4\sqrt{6}\pi^2}{243} N^{3/2} \alpha^6 \left(\ln \left(1 + \frac{4\pi p^2 \phi}{3k_B T v \varepsilon} \right) - \frac{\frac{4\pi p^2 \phi}{3k_B T v \varepsilon}}{1 + \frac{4\pi p^2 \phi}{3k_B T v \varepsilon}} \frac{\varepsilon_s}{\varepsilon} \right). \end{aligned} \quad (6)$$

The first term in the right hand side of eq. (6) determines the influence of volume interactions (excluded volume and Van der Waals interactions) on the polymer chain conformation. The second term is related to the many-body electrostatic dipole correlations of monomers.

III. ANALYSIS OF EXPANDED COIL REGIME

Before we pass to the numerical analysis of eq. (6), it is interesting to discuss the regime of the expanded coil conformation, i.e., when the expansion factor is $\alpha \gg 1$. In this case we obtain the following equation

$$\alpha^5 - \alpha = \frac{3\sqrt{6}}{2\pi} \sqrt{N} \left(1 - 2\chi - \frac{32\pi^3 p^4}{27(k_B T)^2 \varepsilon_s^2 v^2} + \frac{16\pi^2 p^2}{9k_B T \varepsilon_s v} \delta \right), \quad (7)$$

where the *dielectric mismatch* parameter $\delta = (\varepsilon_s - \varepsilon_p) / \varepsilon_s$ is introduced. Thus, for the coil conformation one can introduce the second virial coefficient of the monomer-monomer interactions as follows:

$$B = v \left(\frac{1}{2} - \chi \right) - \frac{16\pi^3 p^4}{27(k_B T)^2 \varepsilon_s^2 v} + \frac{8\pi^2 p^2}{9k_B T \varepsilon_s} \delta. \quad (8)$$

The first term in the right hand side of (8) is a second virial coefficient within the FH theory⁵⁶. The second term is a contribution of the Keesom dipole-dipole interaction⁵⁹ which is always negative value^{33,36,44}. The third term is related to a dielectric mismatch between the pure solvent and polymeric material. The sign of the latter contribution is determined by the sign of the mismatch parameter δ . Thus, effect of dielectric mismatch competes with the Keesom attraction between monomers, when the condition $\varepsilon_s > \varepsilon_p$ ($\delta > 0$) is satisfied. In other words, dielectric mismatch effect tends to expand the polymer coil, whereas the Keesom monomer-monomer attraction, oppositely, provokes its shrinking. The latter can be interpreted as follows. In case of $\delta > 0$ an electric charge of the permanent dipoles is preferentially solvated by the solvent molecules that leads to effective repulsive interaction between monomers. In the opposite case of $\varepsilon_s < \varepsilon_p$ ($\delta < 0$) both Keesom interaction and dielectric mismatch effect lead to collapse of the polymer coil. In this case the electric charge of permanent dipoles tends to be solvated by the monomers instead the solvent molecules that leads to additional effective attractive interaction between monomers. This is an example of manifestation of the so-called solvation forces⁵⁷. It should be noted that only at $\delta \leq (\varepsilon_s - 1) / \varepsilon_s$ (where $\varepsilon_s \geq 1$) the physical condition⁵⁸ for the dielectric permittivity of polymeric material $\varepsilon_p \geq 1$ is fulfilled.

In conclusion of this section it is instructive to write expression for electrostatic free energy in the limit of $\alpha \gg 1$ (or $\phi \ll 1$):

$$F_{el} \simeq \frac{8\pi^2 N p^2}{9\varepsilon_s v} \left(\delta - \frac{2\pi p^2}{3k_B T \varepsilon_s v} \right) \phi, \quad (9)$$

where we have omitted the term which does not depend on the gyration radius. The latter relation determines electrostatic free energy of polymer coil at the level of pairwise correlations.

Therefore, one can conclude that dipole electrostatic correlations of monomers can be taken into account as pairwise only when the polymer chain is in the coil conformation.

IV. NUMERICAL RESULTS AND DISCUSSIONS

Turning to a numerical analysis of (6), we define the following "coupling" parameter

$$\lambda = \frac{p^2}{3\varepsilon_s v k_B T}$$

which determines a "strength" of the dipole electrostatic correlations of monomers. In this study we shall consider only the case of good solvent ($\chi \leq 1/2$). Fig. 2 demonstrates the dependences of the expansion factor α on the coupling parameter λ at different values of dielectric mismatch parameter δ . In region of $\delta > 0$ ($\varepsilon_s > \varepsilon_p$) one can see the pronounced maximum on the expansion factor curve. This maximum is caused by the mentioned above competition of the Keesom dipole-dipole attraction and effective repulsion between monomers attributed to difference between the bulk and local dielectric permittivities (see the discussion in Section 3). For negative δ the expansion factor monotonically decreases at increasing the coupling parameter. In both cases at the large enough coupling parameter the CG transition proceeds continuously.

Now we would like to compare the results obtained by present theory with those predicted by the theory with the pairwise dipole correlations (see, for instance,^{33,36}). It should be noted, that within such theory the electrostatic contribution to the free energy may be assessed by the relation (9). As it is depicted in Fig. 3, accounting for the dipole correlations at the many-body level leads to qualitatively different dependence of the expansion factor on the coupling parameter. Indeed, accounting for the dipole correlations at the pairwise level results in an abrupt decrease of the expansion factor, when the coupling parameter exceeds some threshold value. However, accounting for the higher dipole correlations makes the CG transition smoother.

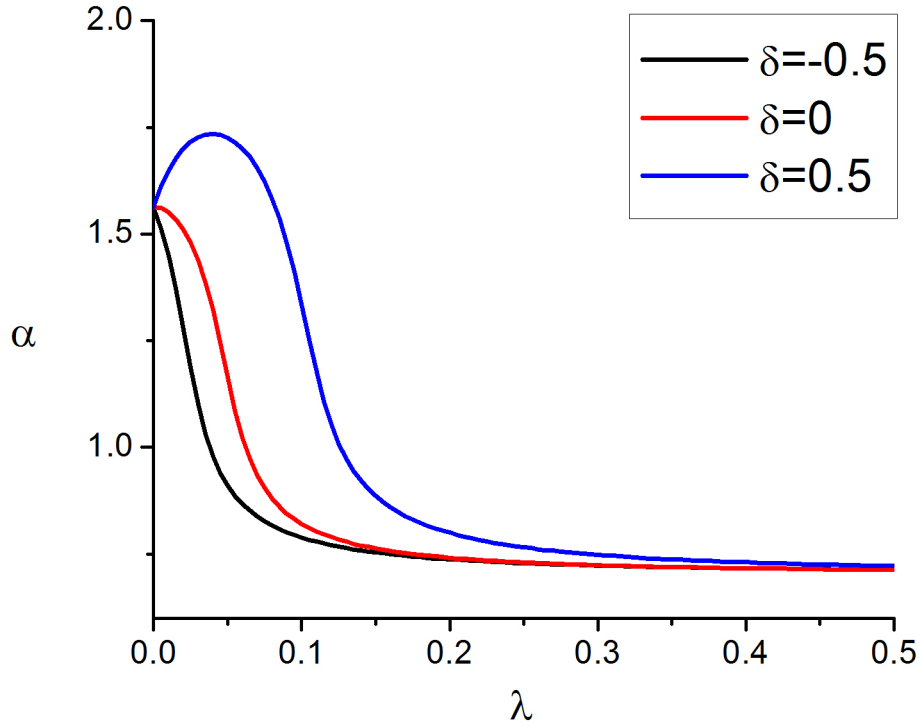


Figure 2. The dependences of expansion factor α on the coupling parameter $\lambda = p^2/(3\varepsilon_s v k_B T)$ at the different values of dielectric mismatch parameter $\delta = (\varepsilon_s - \varepsilon_p)/\varepsilon_s$. The data are shown for $N = 100$, $\chi = 0.2$.

V. CONCLUDING REMARKS

In conclusion, we have formulated a simple analytical self-consistent field theory of flexible polymer chain dissolved in a good solvent, whose monomers carry the permanent freely oriented dipoles. Such effects as dipole correlations at the many-body level and effect of the dielectric heterogeneity near the polymer backbone (*dielectric mismatch* effect) have been taken into account. We have shown that in the regime of good solvent strong enough electrostatic dipole correlations of monomers lead to coil-globule transition. However, in contrast to the theory with pairwise dipole correlations, predicting the coil-globule transition as a first-order phase transition³⁶, present many-body level theory describes the conformational transition as a continuous process. We have demonstrated that the dipole correlations of monomers can be taken into account as pairwise only when the polymer chain is in the

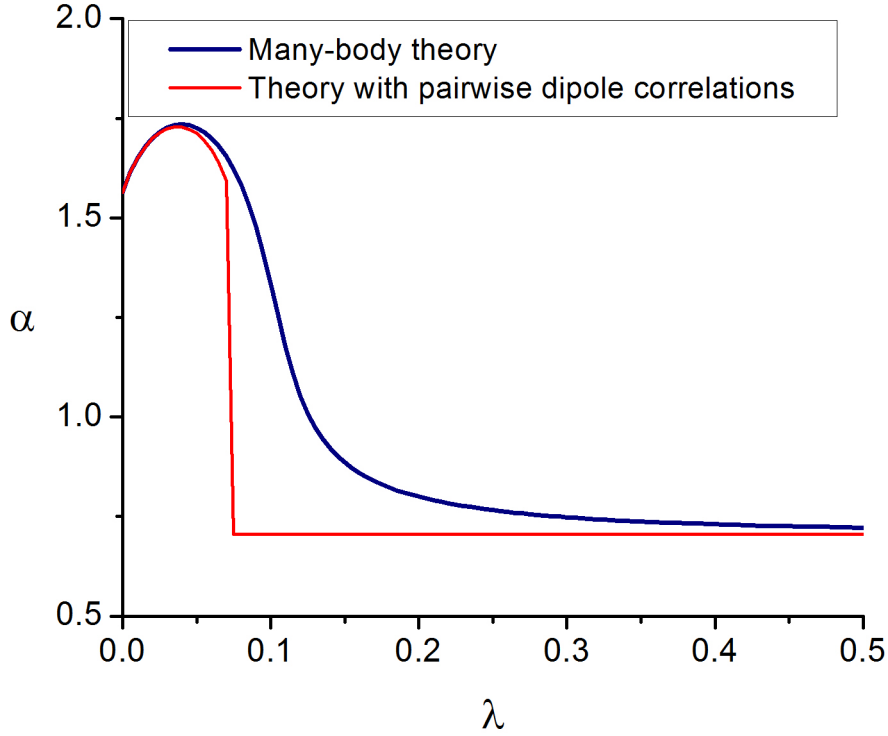


Figure 3. The dependences of expansion factor α on the coupling parameter $\lambda = p^2/(3\varepsilon_s v k_B T)$ calculated within the present theory and theory with pairwise dipole correlations of monomers. Accounting for the dipole correlations at the many-body level makes the coil-globule transition induced by dipole correlations smoother. The data are shown for $\delta = 0.5$, $\chi = 0.2$ and $N = 100$.

coil conformation. For the globular conformation dipole correlations have to be taken into account at the many-body level. We have shown that in the case, when the dielectric permittivity of solvent larger than permittivity of polymeric material, the dielectric mismatch effect competes with the electrostatic dipole correlations of monomers, expanding the polymer coil. In opposite case, when the dielectric permittivity of the polymeric material exceeds the permittivity of the solvent, both effects dielectric mismatch and electrostatic dipole correlations lead to the polymer chain collapse.

It should be noted that in present study in contrast to the papers^{39,42} (where the dielectric permittivities were calculated within the mean-field theory), we introduce the reference dielectric permittivities for the solvent and polymeric material as the free parameters of the model. The latter is due to the fact that all existing "first-principle" analytical approaches

for the dielectric permittivity calculation cannot give satisfactory agreement with the experimental values without introducing some additional fitting parameters^{50–52}. Moreover, the static dielectric permittivities of real liquid-phase solutions are determined by many different physical effects, including the electronic polarizability, thermal orientational fluctuations of the permanent dipoles, hydrogen bonding, etc. It is evident that all of these effects cannot be properly taken into account simultaneously within some analytical theory. Therefore, in our opinion, for the phenomenological description of thermodynamic and conformational properties of polyelectrolytes and polar polymers dissolved in some dielectric solvent it is most naturally to introduce the dielectric permittivities of solvent and polymeric material as the free model parameters.

Finally we would like to discuss the possible applications of present theoretical model. Firstly, it can be used as a theoretical background for analysis of conformational behavior of weak polyelectrolyte chains in the regime of counterion condensation or polyzwitterionic macromolecules in the dilute solutions. Secondly, this theory might be combined with theory of polyelectrolyte chain collapse induced by the electrostatic correlations of counterions^{20,24}. Moreover, it is interesting to find and study a "crossover" region between the Coulombic and dipole regimes of the CG transition of polyelectrolyte chain. The latter is a subject of forthcoming publications.

VI. APPENDIX: DERIVATION OF ELECTROSTATIC FREE ENERGY (4)

Here we present a derivation of electrostatic contribution (4) to the solvation free energy of the polymer chain, which is related to the monomer dipole correlations. We would like to stress that theory which will be presented below can be applied to both single long enough polar polymer chain and concentrated solution of overlapped polar polymer chains.

The electrostatic contribution can be expressed via the electrostatic partition function

$$Q_{el} = \left\langle \exp \left[-\frac{1}{2k_B T} \int_V d\mathbf{r} \int_V d\mathbf{r}' \hat{\rho}(\mathbf{r}) G_0(\mathbf{r}, \mathbf{r}') \hat{\rho}(\mathbf{r}') \right] \right\rangle, \quad (10)$$

as follows

$$F_{el} = -k_B T \ln Q_{el}, \quad (11)$$

where the operator-inverse $G_0(\mathbf{r}, \mathbf{r}')$ with respect to the operator

$$G_0^{-1}(\mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi} \nabla (\varepsilon(\mathbf{r}) \nabla \delta(\mathbf{r} - \mathbf{r}')) \quad (12)$$

and the microscopic dipole charge density

$$\hat{\rho}(\mathbf{r}) = - \sum_{j=1}^N \mathbf{p}_j \nabla \delta(\mathbf{r} - \mathbf{r}_j) \quad (13)$$

are introduced; $\varepsilon(\mathbf{r})$ is the reference dielectric permittivity of medium, which is not related to the permanent dipoles of monomers; symbol $\langle \dots \rangle$ means the average over the orientations of noninteracting permanent dipoles and the positions of monomers.

Using the standard Hubbard-Stratonovich transformation, we rewrite the electrostatic partition function as the following functional integral

$$Q_{el} = \int \frac{\mathcal{D}\psi}{C} \exp \left[-\frac{k_B T}{2} (\psi, G_0^{-1} \psi) \right] \langle \exp [i (\hat{\rho}, \psi)] \rangle, \quad (14)$$

where the short-hand notations

$$(\psi, G_0^{-1} \psi) = \int_V d\mathbf{r} \int_V d\mathbf{r}' \psi(\mathbf{r}) G_0^{-1}(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}'), \quad (15)$$

and

$$(\hat{\rho}, \psi) = \int_V d\mathbf{r} \hat{\rho}(\mathbf{r}) \psi(\mathbf{r}) \quad (16)$$

are introduced; $C = \int \mathcal{D}\psi \exp \left[-\frac{k_B T}{2} (\psi, G_0^{-1} \psi) \right]$ is the normalization constant.

Applying the standard cumulant expansion in integrand of (14) and truncating it at second order, we obtain

$$\begin{aligned} \langle \exp [i (\hat{\rho}, \psi)] \rangle &= \exp \left[i \int_V d\mathbf{r} \langle \hat{\rho}(\mathbf{r}) \rangle_c \psi(\mathbf{r}) - \frac{1}{2} \int_V d\mathbf{r} \int_V d\mathbf{r}' \langle \hat{\rho}(\mathbf{r}) \hat{\rho}(\mathbf{r}') \rangle_c \psi(\mathbf{r}) \psi(\mathbf{r}') + \dots \right] \\ &= \exp \left[-\frac{1}{2} \int_V d\mathbf{r} \int_V d\mathbf{r}' \sum_{i=1}^N \sum_{j=1}^N \langle \mathbf{p}_i^\alpha \mathbf{p}_j^\gamma \rangle \langle \nabla_\alpha \delta(\mathbf{r} - \mathbf{r}_i) \nabla_\gamma \delta(\mathbf{r}' - \mathbf{r}_j) \rangle \psi(\mathbf{r}) \psi(\mathbf{r}') + \dots \right] \\ &= \exp \left[-\frac{p^2}{6} \sum_{j=1}^N \langle (\nabla \psi(\mathbf{r}_j))^2 \rangle + \dots \right] = \exp \left[-\frac{p^2}{6} \int_V d\mathbf{r} \langle \hat{n}_m(\mathbf{r}) \rangle (\nabla \psi(\mathbf{r}))^2 + \dots \right], \end{aligned} \quad (17)$$

where the relations $\langle \hat{\rho}(\mathbf{r}) \rangle = 0$ and $\langle \mathbf{p}_i^\alpha \mathbf{p}_j^\gamma \rangle = p^2 \delta_{\alpha\gamma} \delta_{ij} / 3$ ($\alpha, \gamma = 1, 2, 3$ and $i, j = 1, \dots, N$) have been taken into account and the microscopic monomer density $\hat{n}_m(\mathbf{r}) = \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j)$ has been introduced; symbol $\langle \dots \rangle_c$ means the cumulant average⁶⁰; $\delta_{\alpha\gamma}$ and δ_{ij} are the Kronecker delta.

Therefore, at the level of Gaussian approximation we obtain

$$Q_{el} \approx \int \frac{\mathcal{D}\psi}{C} \exp \left[-\frac{k_B T}{2} (\psi, G_0^{-1} \psi) \right] \exp \left[-\frac{p^2}{6} \int_V d\mathbf{r} \langle \hat{n}_m(\mathbf{r}) \rangle (\nabla \psi(\mathbf{r}))^2 \right]$$

$$= \int \frac{\mathcal{D}\psi}{C} \exp \left[-\frac{k_B T}{2} (\psi, G^{-1} \psi) \right] = \sqrt{\frac{\det G_0^{-1}}{\det G^{-1}}}, \quad (18)$$

where the operator

$$G^{-1}(\mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi} \nabla (\varepsilon_r(\mathbf{r}) \nabla \delta(\mathbf{r} - \mathbf{r}')), \quad (19)$$

and renormalized dielectric permittivity^{61,62}

$$\varepsilon_r(\mathbf{r}) = \varepsilon(\mathbf{r}) + \frac{4\pi p^2}{3k_B T} \langle \hat{n}_m(\mathbf{r}) \rangle \quad (20)$$

have been introduced.

In the case of large enough system volume ($V \rightarrow \infty$) and homogeneous dielectric medium ($\varepsilon(\mathbf{r}) = \varepsilon = \text{const}$) neglecting the boundary effects, we get the following assess for the electrostatic free energy

$$F_{el} \simeq -\frac{V k_B T}{2} \int_{|\mathbf{k}| < \Lambda} \frac{d\mathbf{k}}{(2\pi)^3} \ln \left(\frac{G(\mathbf{k})}{G_0(\mathbf{k})} \right), \quad (21)$$

where $G_0(\mathbf{k}) = 4\pi/(\varepsilon \mathbf{k}^2)$ and $G(\mathbf{k}) = 4\pi/(\varepsilon_r \mathbf{k}^2)$ are the Fourier-images of the Green functions of Poisson equation for the infinite space; $\varepsilon_r = \varepsilon + 4\pi p^2 n_m / (3k_B T)$ is the renormalized dielectric permittivity; $n_m = \langle \hat{n}_m(\mathbf{r}) \rangle = N/V$ is the average monomer number density; $\Lambda = 2\pi/b$ is the parameter of ultraviolet cut-off. The choice of such value of the cut-off parameter Λ is motivated by the fact that at the scales $\sim b$ there are no fluctuations of the electrostatic potential related to the thermal orientation fluctuations of dipoles³⁸. Using the above expressions, we obtain eventually

$$F_{el} \simeq \frac{2\pi V k_B T}{3b^3} \ln \left(1 + \frac{4\pi p^2 n_m}{3k_B T \varepsilon} \right). \quad (22)$$

Expression (22) determines the electrostatic contribution to the total free energy of polymer solution related to the dipole electrostatic correlations of monomers at the level of Gaussian approximation (RPA).

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